SYNTHESIS AND THE SPECTRAL INVESTIGATIONS OF SPIRO, ANSA AND BRIDGED DERIVATIVES OF CYCLOCHLOROTRIPHOSPHAZENES

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ÖZET

Bu çalışmada, 2,2-dimetilpropan-1,3-diol ile trimer, $N_3P_3Cl_6$ (1) reaksiyona sokularak, monospiro, $N_3P_3Cl_4[(OCH_2)_2\text{-}CMe_2]$ (3); dispiro, $N_3P_3Cl_2[(OCH_2)_2\text{-}CMe_2]_2$ (5), ve tri-spiro, $N_3P_3Cl[(OCH_2)_2\text{-}CMe_2]_3$ (7); dangler $N_3P_3Cl_5[(OCH_2)_2\text{-}CMe_2OH]$ (8); mono anza, $N_3P_3Cl_4[(OCH_2)_2\text{-}CMe_2]$ (8) ve spiro-anza $N_3P_3Cl_2[(OCH_2)_2\text{-}CMe_2]_2$ (6) izomerleri; mono-, $N_3P_3Cl_5[(OCH_2)_2\text{-}CMe_2]N_3P_3Cl_5$ (9); di-, $N_3P_3Cl_4[(OCH_2)_2\text{-}CMe_2]_2N_3P_3Cl_4$ (10) ve tri-bino, $N_3P_3Cl_3[(OCH_2)_2\text{-}CMe_2]_3N_3P_3Cl_3$ (11) türevlerinden oluşan 9 adet yeni siklofosfazen bileşiği elde edilmiştir. Ürünlerin türü ve oranları, propan-1,3-diol reaksiyon sistemi ile karşılaştırılmıştır. 2,2-dimetil-propan-1,3-diol'dan elde edilen bileşik türleri ve oranları metil grubu taşımayan analoglara göre önemli ölçüde artmıştır. Elde edilen bileşiklerin yapıları ^{31}P, ^{1}H ve ^{13}C NMR spectrumları verilerinden faydalanılarak karakterize edilmiştir.

Anahtar Kelimeler: sikloklorotrifosfazatrien; bis(2-hidroksietil)eter; spiro bileşikleri; ansa bileşikleri; dangling türevi;bino-bileşikleri; N.M.R. verileri.

ABSTRACT

The reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ (1) with 2,2-dimethylpropane-1,3-diol yield 9 new cyclophosphazene derivatives. One monospiro, $N_3P_3Cl_4[(OCH_2)_2\text{-}CMe_2]$, dispiro, $N_3P_3Cl_2[(OCH_2)_2\text{-}CMe_2]_2$ and tris-spiro $N_3P_3[(OCH_2)_2\text{-}CMe_2]_3$ derivatives. An ansa, $N_3P_3Cl_4[(OCH_2)_2\text{-}CMe_2]$, and a spiro-ansa, $N_3P_3Cl_2[(OCH_2)_2\text{-}CMe_2]_2$ isomers. One dangling, $N_3P_3Cl_5[(OCH_2)_2\text{-}CMe_2OH]$, one singly-bridged, $N_3P_3Cl_5[(OCH_2)_2\text{-}CMe_2]$ $N_3P_3Cl_5$, one doubly-bridged, $N_3P_3Cl_4[(OCH_2)_2\text{-}CMe_2]_2N_3P_3Cl_4$, and one triple-bridged compounds, $N_3P_3Cl_3[(OCH_2)_2\text{-}CMe_2]_2N_3P_3Cl_3$ were also isolated. Product types and relative yields were compared with those arising from propane-1,3-diol. The yields of the spiro, ansa and the bridged products from the reactions of the dimethylpropane-diol system seem to be considerably enhanced relative to those of its unmethylated analogue. The structures of the compounds were determined by using the data obtained from ^{31}P, ^{1}H and ^{13}C N.M.R.

Key words: hexachlorocyclotriphosphazatriene; 2,2-dimethylpropane-1,3-diol; spiro compounds; ansa compounds; dangling derivative; bridge compounds. N.M.R. studies.

1. INTRODUCTION

We have reported the reactions of hexachlorocyclotriphosphazatriene, $\mathbf{N_3P_3Cl_6}$ (**1**) with ethanediol, propane-1,3-diol and butane-1,4-diol [1,2]. Spiro derivatives were the most prevalent products. These contained, with the above reagents, 5-, 6-, and 7-membered phosphate rings. In a number of these the ***OCH₂*** protons, and where appropriate, the ***CCH₂*** protons were in different chemical environments. Differences in chemical shifts of these methylene protons were only pronounced in the 6-membered phosphate rings, and these proved most useful for structural assignments. The very complexity of their ^{1}**H NMR** spectra required heteronuclear and homonuclear decoupling techniques to extract the relevant parameters. The widths of these signals were, however, in some cases too large for satisfactory homonuclear decoupling , and applied particularly to the decoupling of the ***CCH₂*** protons [8,9,10]. We have therefore studied the reactions of compound (1) with 2,2-dimethylypropane-diol. Not only are the ***CCH₂*** proton signals much less complicated than those with propane-1,3-diol derivatives, but in addition the ***CCH₃*** groups give rise to single line, and hence different environments are more readily detected. Though the inductive affects of the methyl groups the methylated diol should be a somewhat stronger nucleophile than its unmethylated analogue. As a corollary, the presence of the methylated spiro ring should be somewhat more deactivating than its unmethylated counterpart, towards further $\mathbf{S_N2}$ type of attack. Additionally the effects of the gem-dimethyl groups are well known, viz. the Thope-Ingold effects [3]. We have therefore wished to examine the effects, if any, of the above structural changes of the diol on the type and the quantity of products produced, such as spiro (6-membered ring), ansa (8-membered ring), bridging and monodenate derivatives.

2. EXPERIMENTAL

2.1. Materials

Chemicals were obtained as follows:
Reagent grade solvents were used through the work, benzene, light petroleum (b.p. 40-60 ^{0}C), anhydrous diethyl ether (May and Baker Ltd.), 1,4-dioxane (Fisons Scientific Apparatus), deuteriated solvents for n.m.r. spectroscopy, 2,2-dimethylpropane-1,3-diol (Aldrich Chem. Co. Ltd.), pyridine, dichloromethane (B.D.H. Chemical Co. Ltd.), hexachlorocyclotriphosphazatriene (Shin Nisso Kako Co. Ltd.). Solvents were dried by conventional methods.

2.2. Methods

All reactions were monitored by using Kieselgel 60^0 254 (silica gel) precouted t.l.c. plates and sprayed with Ninhydridine (0,5 % w/v) in butanol solution, and developed at approximately 130 ^{0}C. Separation of products were carried out by flash column chromatography^9 using Kiesellgel 60. Melting points were determined on a Reichart-Kofler micro heating stage and a mettler FB 82 hot stage connected to a FP 800 central processor both fitted using with a polarising microscope. $^{\mathbf{1}}$**H** n.m.r. spectra were recorded using a JEOL FX-200 spectrometer (operating at 199.5 MHz.), a Bruker WH 250 spectrometer (operating at 250.48 MHz. -King's College, London) and a Varian XL-400 spectrometer (operating at 399.5 MHz. University College, London). Samples were dissolved in $CDCl_3$ and placed in 5mm. n.m.r. tubes. Measurements were carried out using a $CDCl_3$ lock, T**MS** as internal reference and sample concentrations of 15-20 mg cm^3. $^{\mathbf{31}}$**P** n.m.r. spectra were recorded using a Varian XL-200 spectrometer (operating at 80.96 MHz. - University College London), a Varian 400 spectrometer (operating at 162.0 MHz. -University College, London); 85% $\mathbf{H_3PO_4}$ was used as an internal reference. $^{\mathbf{13}}$**C** n.m.r. spectra were recorded using a JEOL FX-200 spectrometer (operating at 50.10 MHz.) and a Varian VXR 400 spectrometer (operating at 100.577 MHz. -University College, London) **TMS** was used as an internal reference. The mass spectra were recorded using a VG 7070H Mass Spectrometer with Finingan INCOS Data System at University College, London and a VG 2AB IF mass spectrometer at the School of Pharmacy. Microanalyses were carried out by University College, London microannalytic service.

2.3. Reactions of cyclochlorotriphosphazenes, $N_3P_3Cl_6$ (1) with 2,3-dimethylpropane-1,3-diol, $[(OCH_2)_2\text{-}CMe_2]$.

(a) One equivalent.

To $\mathbf{N_3P_3Cl_6}$ (9 g, 25.86 mmol) in dioxane (150 cm^3) was added anhydrous pyridine (4.1 g, 51.83 mmol) dropwise as hydrogen chloride acceptor. The 2,2-dimethylpropane-1,3-diol (2.7 g., 25.92 mmol) solution in dioxane (50 cm^3) was added to the trimer solution. After 20 h., the bulk of the pyridine hydrochloride was filtered off, the remainder being removed by column chromatography using a mixture of benzene/dichloromethane (1:6) as eluent. Three main phosphazene fractions were obtained: (**i**) $\mathbf{N_3P_3Cl_6}$, (**ii**) mono spiro derivative (**3**) this and other derivatives, except (**7**) were recrystalised from benzene containing a few drops of light petroleum (b.p. 40-60 ^{0}C), m.p. 157-158 ^{0}C, yield 2.6 g (29 %). [Found: C, 15.90; H, 2.7; N, 11.1%; M$^+$, 377. $\mathbf{C_5H_{10}O_2}$ $\mathbf{N_3P_3Cl_4}$ requires C, 15.85; H, 2.7; N, 11.1 %; M, 377]; (**iii**) the doubly-bridged derivative (**10**), m.p. 178-179 ^{0}C, yield 0.9g (10%). [Found: C, 15.85; H, 2.7, N, 11.1%; (M $^+$ 1) $^+$, 755, C.I. in NH_3. $\mathbf{C_{10}H_{20}O_4}$ $\mathbf{N_6P_6Cl_8}$ requires C, 15.85; H, 2.7; N, 11.1 %; M, 754)].

(b) Two equivalents.

The reaction was carried out as in (**a**) with reflux for 3h. Two phosphazene derivatives were separated by column chromatography using a mixture of C_6H_6/CH_2Cl_2 (1:6) as eluent. (**i**) The bis spiro compound (**5**), m.p. 194-196 ^{0}C, yield 2.2 g (25 %). [Found: C, 29.3; H, 4.9; N, 10.3 %; M$^+$, 409. $\mathbf{C_{10}H_{20}O_4N_3P_3Cl_2}$ requires C, 29.3; H, 4.9; N, 10.2 %; M, 409]; (**ii**) the spiro-ansa isomer (**6**) m.p. 114-116 ^{0}C, yield 0.7 g (8 %). [Found: C, 29.3; H, 5.0; N, 10.3 %; M$^+$, 409. $\mathbf{C_{10}H_{20}O_4N_3P_3Cl_2}$ requires C, 29.3; H, 4.9; N, 10.2 %; M, 409].

(c) Three equivalents.

The same procedure as for (a); the reflux time was 8h. Two major compounds were separated by column chromatography using a mixture of diethyl ether / dichloromethane (1:1) as eluent. (i)The tris-spiro derivative (7) was recrystalised from CH_2Cl_2, m.p. 277-279 ^{0}C, yield 1.8 g (20 %). [Found: C, 43.5; H, 6.9; N, 10.2 %; M$^+$, 441. $C_{15}H_{30}O_6N_3P_3$ requires C, 43.5; H, 6.9; N, 10.2 %; M, 441]. (ii) Dangling derivative (8), m.p. 159 0C, yield 0.33 g (19 %). [Found: C, 14.55; H, 2.7, N; 10.21 %; M$^+$, 413. $C_5H_{11}O_2N_3P_3Cl_5$ requires C, 14.52; H, 2.66; N, 10.16 %; M, 413].

(d) Three equivalents in dichloromethane.

To **(1)** (4g 11.49 mmol) in dichloromethane (100 cm^3) was added dropwise anhydrous pyridine (5.44 g, 68.86 mmol).

2,2-Dimethylpropane-1,3-diol (3.51 g, 34.41 mmol) in dichloromethane (50 cm^3) was then added dropwise. The solution was allowed to stand for 12 h; the bulk of the pyridene hydrochloride was filtered off and the remainder removed by column chromatography. Elution with PhH/CH_2Cl_2 (1:5) gave four known and one new phosphazene derivative. All were recrystalised from PhH containing a few drops of light petroleum (b.p. 40-60 ^{0}C). Order of elution and yield were as follows. (**3**) (24.5 %), (**4**) (36.2 %) m.p. 187 ^{0}C. [Found: C, 15.9; H, 2.6; N, 11.2 %; M$^+$, 377. **$C_7H_{10}O_2$ $N_3P_3Cl_4$** requires C, 15.85; H, 2.7; N, 11.1 %; M, 377], (**6**) (17.1 %), (**5**) (14.1 %) and (**10**) (6.3 %).

(e) Three equivalents in benzene

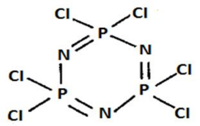
The reaction was carried out as in (**b**) with reflux time for 8h. To **(1)** (4g 11.49 mmol) in benzene (150 cm^3) was added dropwise anhydrous pyridine (5.44 g , 68.86 mmol). 2,2-Dimethylpropane-1,3-diol (3.51 g, 34.41 mmol) in benzene (50 cm^3) was then added dropwise. The solution was allowed to stand for 12 h; the bulk of the pyridene hydrochloride was filtered off and the remainder removed by column Chromatography. Elution with PhH/CH_2Cl_2 (1:5) gave three known and two new products.

All were recrystalised from benzene containing a few drops of light petroleum (b.p. 40-60 ^{0}C), (**i**) an oily product, (**9**), yield 0.7 g (11 %). [Found: C, 8.41; H, 1.39; N, 11.76 %; M$^+$, 722. **$C_5H_{10}O_2N_6P_6Cl_{10}$** requires C, 8.31; H, 138; N, 11.63 %; M, 722]. (**ii**) (**11**) m.p. 248 ^{0}C, [Found: C, 23.11; H, 3.87; N, 10.51 %; M$^+$, 786. **$C_{15}H_{30}O_6N_6P_6Cl_6$** requires C, 22.90: H, 3.81; N, 10.43 %; M, 786].

3. RESULTS AND DISCUSSION

We isolated nine products from the above reaction system: **$N_3P_3Cl_4[(OCH_2)_2\text{-}CMe_2]$** (**3,4**), (two isomers); **$N_3P_3Cl_2[(OCH_2)_2\text{-}CMe_2]_2$** (**5,6**) (two isomers); **$N_3P_3[(OCH_2)_2\text{-}CMe_2]_3$** (**7**); one dangler, **$N_3P_3Cl_5(N_3P_3Cl_5[(OCH_2)_2\text{-}CMe_2OH]$** (**8**); one singly-, **$N_3P_3Cl_5[(OCH_2)_2\text{-}CMe_2]$ $N_3P_3Cl_5$** (**9**); one doubly- **$N_3P_3Cl_4[(OCH_2)_2\text{-}CMe_2]_2N_3P_3Cl_4$**, (**10**) and one triple-bridged, **$N_3P_3Cl_3[(OCH_2)_2\text{-}CMe_2]_2N_3P_3Cl_3$** (**11**) derivatives. We now discuss their structures based on n.m.r. spectroscopic studies.

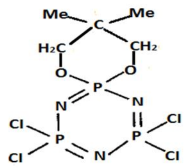
PHOSPHORUS-NITROGEN COMPOUNDS



(1)

(HO-CH_2-CMe_2-CH_2-OH)

(2)



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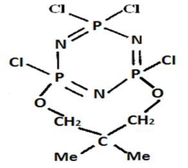

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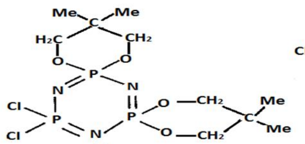

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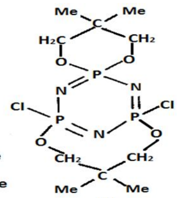

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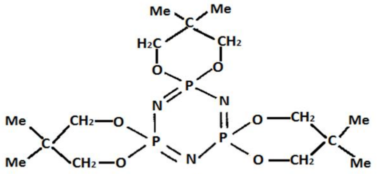

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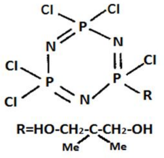

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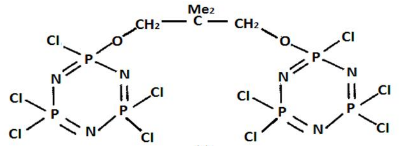

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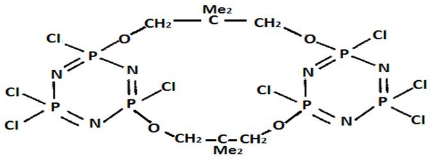

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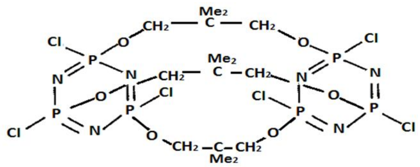

(11)

3.1. ^{31}P N.M.R. Studies

Compounds **(3)** and **(4),** whose analyses and mass spectra showed these to be **$N_3P_3Cl_4[(OCH_2)_2\text{-}CMe_2]$** could have in principle two structures: spiro **(3)** or ansa (**4**). Both types are known for propane-1,3-diol [2], although the ansa compound occurs only in very low yield. Experience with these two isomers shows that the ansa compound has an **A_2B** spectrum, whilst that of the spiro isomer is of the **A_2X** type [11,12,13]. Proton coupling affects the **A_2** part of the former and the **X** part of the latter. The spectrum of compound **(3)** is of the **A_2X** type, with the X part showing further splitting on proton coupling. Thus this compound can be assigned with confidence the spiro structure **(3)**. Its isomer has its **A_2** part affected by proton coupling. It is thus assigned the ansa structure **(4)**. In contrast to the propane diol system, where the yield of the ansa compound is minute and only a fraction of that of its spiro isomer [2], in the present system the yield of the ansa compound **(4)** is somewhat larger than that of its spiro isomer (**3**). The isomeric compound **(5)** and **(6)** both exhibit **A_2X** spectra. Proton coupling experiments as well as comparison with the analogous propane-diol derivatives, allow unambiguous assignments of structures. Compound **(5)** is the dispiro derivative, compound **(6)** its spiro-ansa isomer. The yields of these two isomers **(5)** and **(6)** are comparable in this system, in contrast to that of the unmethylated diol, where the dispiro compound is in larger yield [2]. The sharp singlet observed for **$N_3P_3[(OCH_2)_2\text{-}CMe_2]_3$** demonstrates it to be the tris spiro derivative **(7)**. Dangling derivative: Only one functional group attached to phosphorus atoms, the other is free, this compound, **$N_3P_3Cl_5[(OCH_2)_2\text{-}CMe_2OH]$** has an **$A_2B$** types spectrum, proton coupling affects the **A** parts with further splitting on it, whereas the **B** part remain unaffected, together with chemical shift differences and mass spectrometric results, we assigned this structure to be dangling derivative (**8**). Singly-bridged derivative **$N_3P_3Cl_5[(OCH_2)_2\text{-}CMe_2]N_3P_3Cl_5$ (9)** represents the **A_2B** spectrum, **the B** part giving fine structure on proton coupling [8]. We therefore assign a singly-bridged structure **(9)** to this. The compound of composition **$N_3P_3Cl_4[(OCH_2)_2\text{-}CMe_2]N_3P_3Cl_4$** has an **$A_2B$** spectrum, the A_2 part giving fine structure on proton coupling [11,12,13]. This is assigned as doubly-bridged structure **(10)**. This contains an inner 16-membered ring. Triple-bridged compound has given rise to A_3, spin system. ^{31}P n.m.r. spectra presented a single line, suggesting either this is a tris-spiro (7) or a triple bridged structure. At low or high field strengths, triple-bridged structures give rise to **A_3** spin system, tending to a single line transitions. Our own and other groups' experiences suggest that this structure to be feasible and in that conjunction with the mass spectrum as well as the m.p. point differences makes us put forward a triple bridged structure for this, **$N_3P_3Cl_3[(OCH_2)_2\text{-}CMe_2]_2N_3P_3Cl_3$ (11)** . The **^{31}P** data are summarised in **Table 1.**

Table1. ^{31}P N.M.R. Data of Derivatives (1)-(11)[a]

Compound	**δPsiro[b]**	**δPCl$_2$[b]**	**δP(OR)Cl[b]**
(1)		19.9	
(3)[c] mono-spiro	2.2	23.3	
(5)[d] dispiro	8.7	26.1	
(7) tris-spiro	13.9		
(4)[e] ansa		23.5	25.0
(6)[f] spiro-ansa	9.8		31.8
(8)[g] dangling		23.73	7.11
(9)[h] singly-bridged		24.61	8.13
(10)[i] doubly-bridged		26.4	27.4
(11) triple-bridged			25.22

[a] In $CDCl_3$ (65% phosphoric acid external reference) at 80.95 and 162.0 MHz (room temperature).
[b] In p.p.m.
[c] ^2J(P spiro-PCl_2) 69.3 Hz.
[d] ^2J(P spiro-PCl_2) 70.4 Hz.
[e] ^2J[P(OR)Cl – PCl_2] 64.2 Hz.
[f] ^2J[P spiro – P(OR)Cl] 70.9 Hz.
[g] ^2J[P(OR)Cl-PCI_2]76.3 Hz.
[h] ^2J[P(OR)Cl – PCl_2] 63.5 Hz.
[i] ^2J[P(OR)Cl – PCl_2] 57.6 Hz.
[g] ^2J[P(OR)Cl-PCI_2]76.3 Hz.
[h] ^2J[P(OR)Cl – PCl_2] 63.5 Hz.
[i] ^2J[P(OR)Cl – PCl_2] 57.6 Hz.

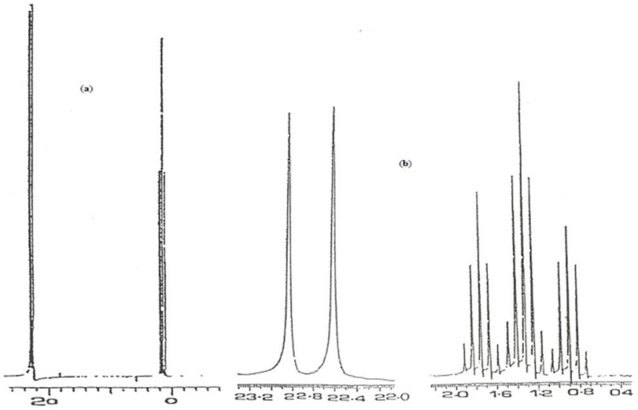

Figure 3.1. ^{31}P N.M.R. spectra of compound (**3**), **$N_3P_3Cl_4[(OCH_2CMe_2CH_2O)]$,** (**a**) proton decoupled, (**b**) proton coupled spectrum, at room temperature, in $CDCl_3$ and at 161.83 MHz.

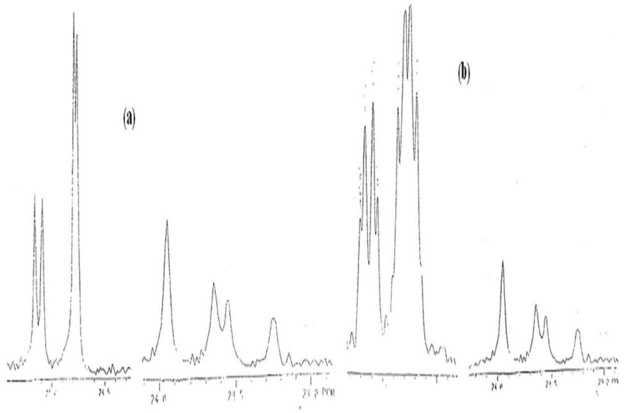

Figure 3.2. ^{31}P N.M.R. spectra of compound (**4**), **$N_3P_3Cl_4$[($OCH_2CMe_2CH_2O$)]**, (**a**) proton decoupled, (**b**) proton coupled spectrum, at room temperature, in $CDCl_3$ and at 160.53 MHz.

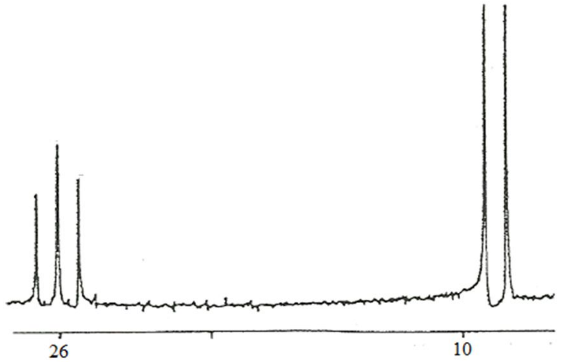

Figure 3.3. ^{31}P N.M.R. proton decoupled spectrum of compound (**5**), **$N_3P_3Cl_2$ [($OCH_2CMe_2CH_2O$)]$_2$**, at room temperature, in $CDCl_3$ and at 162.00 MHz.

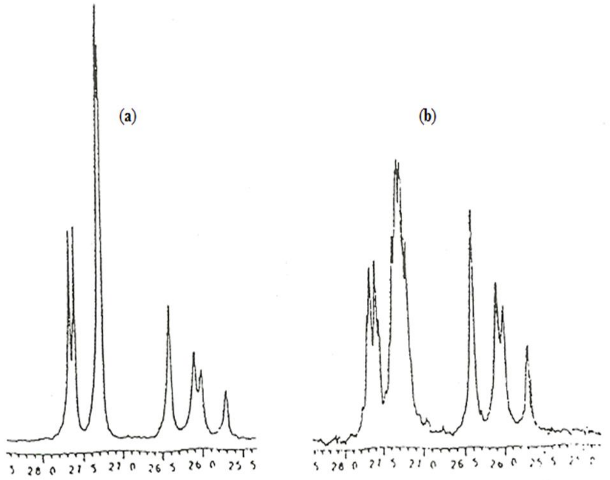

Figure 3.4. ^{31}P N.M.R. spectra of compound (**10**), **$N_3P_3Cl_4$($OCH_2CMe_2CH_2O$)$_2N_3P_3Cl_4$**, (**a**) proton decoupled, (**b**) proton coupled spectrum, at room temperature, in $CDCl_3$ and at 161.83 MHz.

3.2. ^1H N.M.R. Data

These spectra are greatly simplified compared to those of the propane-1,3-diol derivatives [2]. Those of the two spiro derivatives, **$N_3P_3Cl_2[O(CH_2)_3O]_2$** and **$N_3P_3Cl_2(OCH_2CMe_2CH_2O)_3$** are compared in **Figure 6**. The ***OCH_2*** protons are about 0.5 p.p.m. more shielded than those of the corresponding propanediol derivatives. The expected small shielding on passing from mono- to tris-derivative is observed for ***OCH_2*** and to a lesser extent for the ***CH_3*** protons. The ansa **(4)**, the dispiro **(5)**, the ansa portion of the spiro-ansa (**6**) and the doubly-bridged derivative **(10)** show remarkable similarity in ***OCH_2*** and ***CH_3*** in chemical shifts. **$^3J(PH)$** values fall into three distinct groups: **(i)** mono-spiro **(3)**, tris-spiro **(7)** and the spiro section of the spiro-ansa derivative **(6)**; **(ii)** ansa **(3)**, ansa section of compound **(6)** and doubly-bridge derivative **(10)**: **(iii)** dispiro compound **(5)**. The data are in **Table 2**.

Table 2. ^1H N.M.R. Data for Compounds (3-11)[a]

Compound	δOCH_2[b]	δCCH_3[b]	$^3J(PH)$[c]	$^2J(HA\text{-}HB)$
(3)	4.14	1.10	13.2	
(5)	4.20	1.15	5.05	11.9
	3.88	0.99	17.3	
(7)	4.00	1.06	13.1	
(4)	4.22	1.10	7.9	
	3.86	0.98	8.2	11.4
(6) spiro part	4.13	1.05	13.1	
	4.07		13.1	
ansa part	4.20	1.09	7.9	11.8
	3.80	0.95	8.2	
(8)	4.08	1.11	7.95	
(9)	3.98	1.03	8.23	
(10)	4.28	1.07	7.75	
	3.88	0.98	8.8	
(11)	4.03	1.00	8.55	
	3.83	0.92	8.44	

[a] In $CDCl_3$ (TMS internal reference) at 199.5 MHz and 399.95 MHz. (room temperature)
[b] In p.p.m.
[b] In Hz.

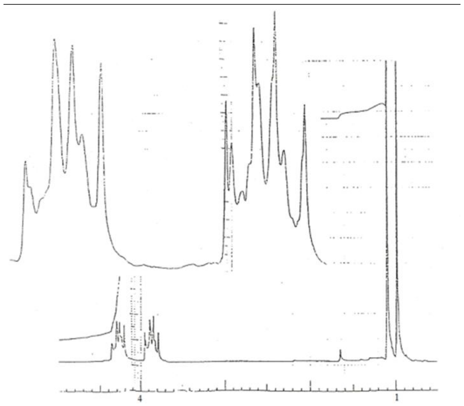

Figure 3.5. ^{1}H N.M.R. spectra of compound (**4**), **$N_3P_3Cl_4$($OCH_2CMe_2CH_2O$),** at room temperature, in $CDCl_3$ and at 199.50 MHz.

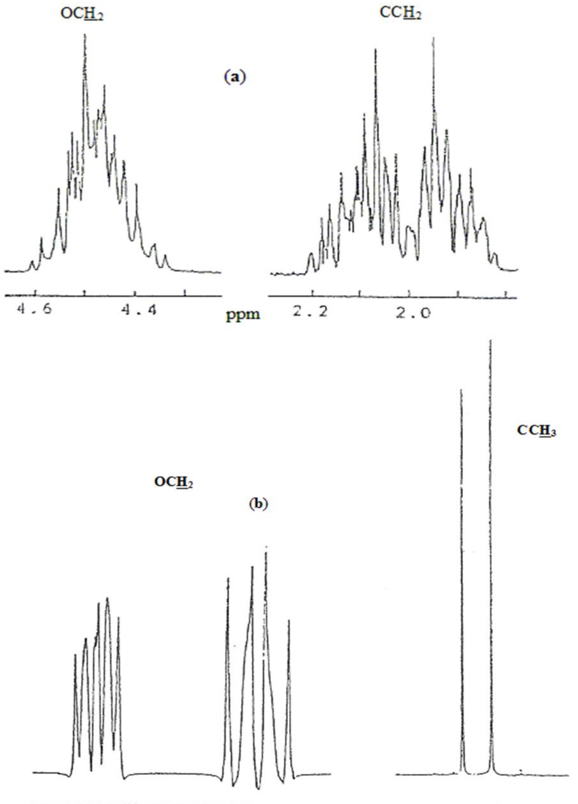

Figure 3.6. Comparison of ^{1}H n.m.r. spectra in $CDCl_3$ at room temperature at 399.95 MHz. (**a**) compound (**5**) **$N_3P_3Cl_2$($OCH_2CMe_2CH_2O$)$_2$** and (**b**) **$N_3P_3Cl_2$ [$O(CH_2)_3O$]$_2$**.

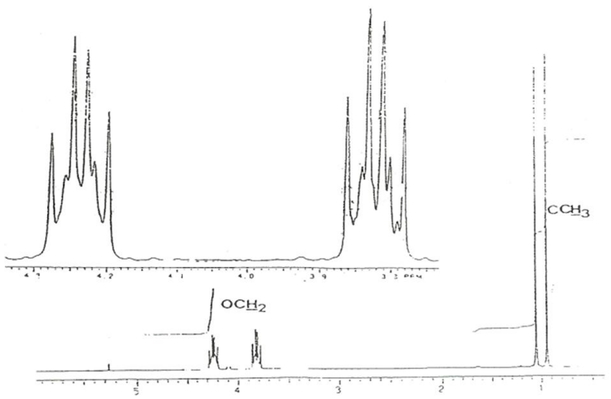

Figure 3.7. ^{1}H N.M.R. spectra of compound (**10**), **$N_3P_3Cl_4$($OCH_2CMe_2CH_2O$)$_2$$N_3P_3Cl_4$** at room temperature, in $CDCl_3$ and at 399.95 MHz.

3.3. ^{13}C n.m.r. Data

In general, three carbon environments are observed except in the case of the spiro-ansa derivative, where separate carbon resonances are observed for the spiro and ansa moieties. The carbon-13 n.m.r. absorbtion for ***PO<u>C</u>H$_2$*** gives rise to a doublet for the mono-spiro derivative due to coupling with the phosphorus nucleus. Virtual coupling effects have been observed in ***PO<u>C</u>H$_2$*** nuclei for the bis-spiro compound. Therefore, these nuclei will couple equally to the carbon nuclei as a result of the identical environments of the phosphorus nuclei; and a triplet structure would be expected for the bis-spiro derivative [n + 1 (n = number of phosphorus nuclei)]. The spectrum of this compound is displayed in **Figure 8**. The ***PO<u>C</u>H$_2$*** spectrum of the spiro-ansa consists of two distinct signals.

In the case of the ansa ring virtual coupling would be expected, since two phosphorus nuclei are linked with identical groups as ansa segment and chlorine atom. Therefore, the triplet structure is assigned to the methylene carbon of the ansa ring, whilst the two carbon nuclei of the ***PO<u>C</u>H$_2$*** groups of the spiro ring show that they are not in identical environments, one carbon faces the chlorine atoms, whereas the second nucleus faces the ansa ring. Thus the two doublets which are observed at 75.97 and 74.50 ppm, respectively belong to the spiro ring. Doublets are also observed for the non-protonated central carbon nucleus ***POC<u>C</u>*** of the mono-spiro and the spiro ring of the spiro-ansa compound due to the direct coupling with the nearest phosphorus nuclei. The ***POC<u>C</u>*** nucleus of the bis-spiro and ansa ring of the spiro-ansa compounds give rise to triplet spectra due to the virtual coupling in the former owing to the identity of the two phosphorus nuclei, and due to the direct coupling in the latter. The methyl carbon signals of the two methyl groups appear as two sharp single lines for compound bis-spiro and ansa part of the spiro-ansa compounds, since these groups are not in identical environments, whereas the absorptions for the same nuclei, for compounds mono-spiro and spiro-ring of the spiro-ansa give rise to single lines owing to the identity of the methyl group environments in these molecules. Assignment of the peaks in the ^{13}C n.m.r. spectra was achieved from the anticipated splitting pattern for each peak and by comparison with the other ansa structures, where the position of the carbon resonance is known, therefore, a triplet structure is observed for the ***PO$\underline{C}$*** region in the spectrum of the ansa structure. These lines are due to direct coupling with the phosphorus nuclei carrying the ansa moiety. For the ***POC$\underline{C}$*** carbon nuclei, a single transition is also observed.

The cabon-13 n.m.r. spectra for the doubly and triple-bridged compounds give the expected triplets for the ***PO$\underline{C}H_2$*** nuclei. This triplet arises from the virtual coupling with two equivalent phosphorus nuclei. Also absorptions for the central carbon are expected to give quintets, since these two equivalent nuclei are linked with equivalent phosphorus nuclei. Thus virtual coupling between these nuclei would give quintet structures.

The normal absorption of ***POC$\underline{C}$*** nuclei were observed as a single line. However, the resolution enhanced spectrum at the same field strength displayed a five line spectrum for those nuclei.

It has been reported [4,5,6] that the three-bond coupling constant values ***$^3\underline{J}(PXC\underline{C})$*** (x= NH or O) are dependent on many factors such as the P-N or P-O bond length, the structure of the hybridisation of the nitrogen or oxygen atom, as well as the dihedral angle ***PXCC*** of the compounds. In the seven-membered ring system the chemical shifts of PXCC were slightly different from those of the six-membered ring systems. The three-bond coupling constants ***$^3\underline{J}(PXC\underline{C})$*** show much larger differences than the chemical shifts, and comparing six- and seven-membered spiro rings, the ***$^3\underline{J}(POC\underline{C})$*** value for the seven-membered rings are zero, in contrast to the six-membered rings, where the corresponding values are approximately 6.4 Hz. In the case of the spiro- ansa compound [2], **$N_3P_3Cl_2[O(CH_2)_3O]_2$**, the ***$^3\underline{J}(POC\underline{C})$*** values for the ansa ring is considerably smaller than that of the spiro ring. The same situation may be assumed for the spiro-ansa compound (**6**). Thus it is clear that the decrease of the ***$^3\underline{J}(POC\underline{C})$*** values in the case of the ansa ring is not due to the P-O bond distance, but is presumably due to the dihedral angles of ***POC$\underline{C}$***. The chemical shift and coupling constants are presented in

Table 3. ^{13}**C N.M.R. data of derivatives (3)-(11)**[a]

Compound		**$\delta PO\underline{C}H_2$** [b]	**$\delta POCH_2\underline{C}$** [b]	**$\delta \underline{C}H$**[b]
(**3**)		77.07	32.18	21.24
(**4**)		74.93	37.07	22.85
				21.09
(**5**)		76.54	32.03	21.74
				20.98
(**6**)	spiro part	76.58	37.09	22.01
	ansa part	74.50	32.03	21.47
				21.39
(**8**)		75.6	31.5	22.4
(**9**)		76.8	32.06	21.91
				21.04
(**10**)		74.95	37.12	21.90
				21.16
(**11**)		75.03	32.91	21.87
				21.70
		$^2\underline{J}(\underline{P}O\underline{C}H_2)$[c]	**$^3\underline{J}(\underline{P}OC\underline{C})$**[c]	
(**3**)		5.9	5.9	
(**4**)		6.9	5.9	
(**5**)		6.5		
(**6**)	spiro rart	6.1	5.9	
	ansa part	7.0	2.2	
(**8**)		6.9	5.8	
(**9**)		7.03	5.8	
(**10**)		6.87	5.7	
(**11**)		6.6	5.5	

[a] In $CDCl_3$ (TMS internal reference) at 50.1 MHz. (room temperature).
[b] In p.p.m. [c] In Hz.

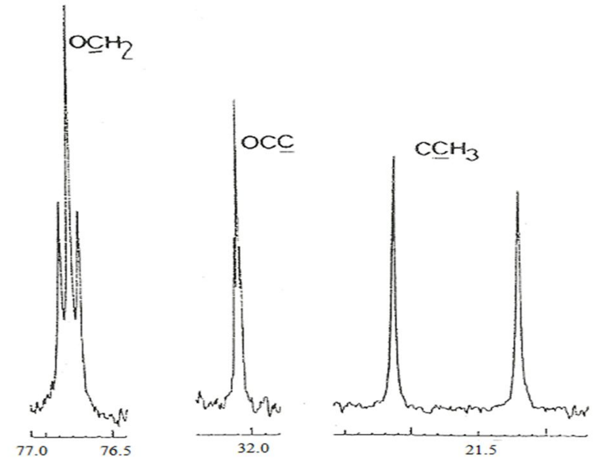

Figure 3.8. ^{13}C N.M.R. spectra of compound (**5**) **$N_3P_3Cl_2(OCH_2CMe_2CH_2O)_2$**, in $CDCl_3$, at room temperature and at 100.53 MHz.

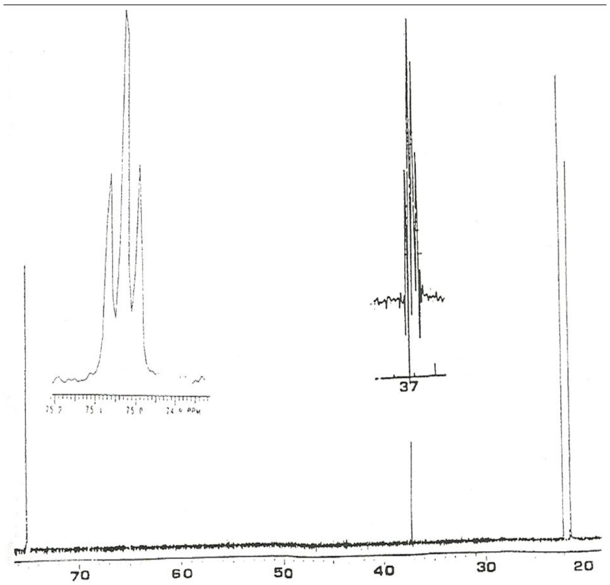

Figure 3.9. ^{1}H N.M.R. spectra of compound (**10**), **$N_3P_3Cl_4(OCH_2CMe_2CH_2O)_2N_3P_3Cl_4$**, at room temperature, in $CDCl_3$ and at 50.1 MHz.

4. SUMMARY

If we consider the present findings pertaining to the reactions of 2,2-dimethylpropane-1,3-diol with the hexachloride (**1**) and compare these with our earlier ones on propane-1,3-diol [2], we note resemblances as well as contrasts. Whilst the latter gave predominantly spiro derivatives (mono, bis, and tris), the **C**-methylated diol gave the yields of mono ansa and spiro-ansa comparable to those of its spiro isomers. Unlike in our earlier studies [1,2] we isolated the first example of doubly-bridge diol derivative with a central 16-membered ring. Doubly-bridged di(primary amino) derivative have been reported by Labarre and co-workers [7]. In their examples the chains linking the two phosphazene rings were considerably larger (8 or 10 atoms) than ours (5 atoms).

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